

⁵¹Int. Cl.*

¹⁹Federal Republic of Germany

⁵²German. Cl.: 39 b5, 20/10

¹⁰**Published Patent Application**
¹¹**DT 2 048 312**

²¹Application Number: P 20 48 312.9

²²Application Date: October 1, 1970

⁴³Date issued: April 6, 1972

• Issuance Priority: —

30 Convention Priority

32 Date: —

33 Country: —

31 Application Number: —

54 Designation: Polymers Comprising Lactam Groups

61 Addition to: —

62 Division from: —

71 Applicant: Badische Anilin- & Soda-Fabrik AG, 6700 Ludwigshafen

Representative according to § 16 of the Patent Act

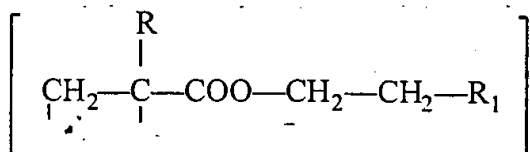
72 Named as Inventor: Willersinn, Herbert, Dr., 6700 Ludwigshafen;
Fürst, Ernst, Dr., 6730 Neustadt;
Naarmann, Herbert, Dr., 6700 Ludwigshafen

* not legible (top of page missing)

Translator: Andrea-Ingrid Schneider, 715-549-5734 (German #586/1997)

Polymers Comprising Lactam Groups

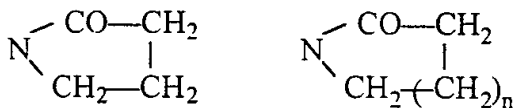
The invention concerns polymers containing lactam groups which are built entirely or in part of monomer units of the general formula



(I)

in which R represents hydrogen or a methyl group and R₁ a lactam group.

Preferably, R₁ consists of a lactam residue of the formula

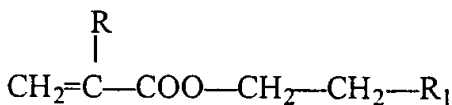


n = 1 to 9.

It is known that vinyl groups that do not comprise amino groups can be easily polymerized.

On the other hand, vinyl groups with amino or ammonium groups, e.g., allyl amine or butene-(1)-amine(3), can under normal conditions practically not be polymerized into high-molecular substances. Secondary or tertiary amines also create difficulties during polymerization, since they could act as chain-transfer agents, or instead, as activators for the radical initiation.

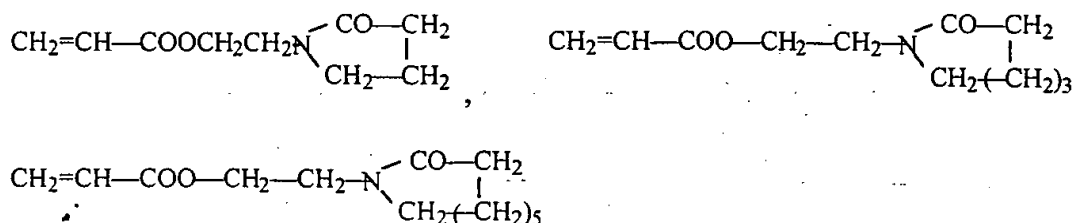
It has now been found that new polymers containing lactam groups are obtained if one polymerizes derivatives of the general formula



(II)

¹ BASF

in which R represents hydrogen or a methyl group and R₁ an imido residue, possibly together with other olefinic unsaturated monomers, in the presence of radical forming initiators and then possibly modifies the residue R₁ according to usual reactions. According to the process of the invention it is now possible to prepare high-molecular substances that comprise lactam groups. Due to the lactam group, such polymers have color-affinity and available for further reactions, e.g., cleavage and cross-linking.



for example, are suitable unsaturated amine derivatives. Such derivatives can be prepared, for example, through the conversion of hydroxyethyl derivatives with acrylic acid- or methacrylic acid esters. The preparation of the new, unsaturated derivatives is not [an] object of this invention.

Suitable olefinic unsaturated monomers which possibly can be copolymerized with the imido derivatives are, for example, olefins, such as ethylene, butadiene, isoprene, styrene and substituted styrenes, such as α -methyl styrene, p-chlorostyrene and p-methylstyrene; acrylic esters and methacrylic esters, in particular those with 1 to 18, preferably 1 to 8 carbon atoms in the alcohol residue, for example, acrylic or methacrylic esters of methanol, ethanol, butanol or ethyl cyclohexanol; acryl- or methacrylamide and substituted amides, such as N-methylol acrylamide, N-methylol methacrylamide or their ethers, such as N-methylol acrylamide butyl ether, N-methylol methacrylamide methyl ether; acrylo- and methacrylonitrile; vinyl esters, such as vinyl acetate, vinyl propionate; vinyl ethers, such as methyl-, ethyl- or alkyl vinyl ethers with alkyl residues with 3 to 6 carbon atoms, furthermore, fumaric, maleic or itaconic acid, esters of these acids and maleic anhydride. Of the compounds mentioned previously, two or several may also be copolymerized simultaneously with the imido derivatives.

For the preparation of the copolymers, the portion of unsaturated amino derivatives in the monomer mixture may vary within broad limits, for example, between 1 and 99, in particular between 10 and 90%.

Regular radical forming initiators are used to initiate the polymerization. Suitable initiators are, for example, hydrogen peroxide, organic hydroperoxides and peroxides, such as

caproyl peroxide, lauroyl peroxide, t-butyl perbenzoate, dicumyl peroxide, p-menthan hydroperoxide, cumene hydroperoxide, succinic peroxide, furthermore, aliphatic azo compounds [which] under polymerization conditions break down into radicals, such as 2,2'-azo-bis-2,4-dimethyl valeronitrile, 2,2'-azo-bis-isobutyronitrile and analogous azonitriles which are presented, for example, in J. Hine "Reaktivität und Mechanismus in der organischen Chemie" ² Verlag Georg Thieme³, Stuttgart (1960), page 412, as well as redox catalyst systems, such as the systems potassium or ammonium sulfate and ascorbic acid, sodium hydrosulfite or iron-II salts.

Further suitable are the chelates of transitional metals known as radical formers, in particular those in which the metal is present with an unusual valency, such as chelates of manganese(III), cobalt(III), copper(II) and cerium(IV). In general, 1,3-dicarbon compounds are used as chelate formers. Manganese(III)-acetyl carbonate and cobalt(III) acetoacetic ester shall be mentioned as examples.

In general, the initiators are used in an amount of 0.05 to 5 percent by weight relative to the amount of monomer. The optimum amount and the optimally effective initiator can be easily determined through experiments.

The polymerization can be performed solventless. But advantageously, one works in the presence of solvents or diluting agents. Suitable are, for example, alcohols, such as methanol, ethanol, propanol or butanol; ketones, such as methyl ethyl- or methyl propyl ketone; ethers, such as tetrahydrofuran or dioxane; aliphatic, cycloaliphatic or aromatic hydrocarbons, such as heptane, hexane, cyclohexane or benzene, also well suitable are formamide and dimethyl formamide; water is used advantageously as diluting agent.

The suspension, solvent or emulsion polymerization processes usual for a variety of other monomers or monomer mixtures are also suitable for the new process. The new process does not differ from known ones also with regard to the possibly used supplementary agents, such as buffer substances, dispersing agents, protective colloids and the like. The polymerization may be performed in a broad temperature range of about between 0 and 150, preferably between 50 and 120°C. One generally works at atmospheric pressure, but lower or higher pressure, for example, up to 3000 atmospheres above atmospheric pressure, may also be used. The use of higher pressures is indicated in particular when

² Reactivity and Mechanism in the Organic Chemistry

³ publisher

using low-boiling comonomers, in order to achieve a sufficient concentration of the comonomers in the reaction mixture.

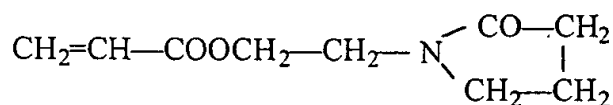
The copolymerization of unsaturated lactam derivatives with ethylene or butadiene is advantageously performed in [an] emulsion in that monomers that copolymerize with one another are introduced into an aqueous soap emulsion that comprises an initiator, a buffer system and possibly a protective colloid, and polymerized at elevated pressure, about up to 2000 atmospheres above atmospheric pressure. Usefully, the copolymerization with acrylic esters is performed in aromatic or aliphatic hydrocarbons under the conditions known for the polymerization of acrylic esters.

The polymers can be used, for example, for the production of molded articles, coatings or adhesives, also in mixtures with other synthetic materials, e.g., polyethylene, polypropylene or with mixed polymers of vinyl acetate and ethylene. Due to their surface active and antistatic properties, the prepared polymers according to the invention are, among other [things], also suitable for finishing paper and textiles and, in part, allow cross-linking reactions. The homopolymers obtained through the radical polymerization have intrinsic viscosities (η) in the range of 0.4 to 2.0 dl/g (25°C). Lit. W. R. Sorenson, T. W. Camphell "Preparative Methods of Polymer Chemistry" Intersc. Pub., N.Y.S. 44 (1968).

The copolymers obtained following the process according to the invention are randomly built polymers, the intrinsic viscosities of these polymers lie in the same range as those of the homopolymers.

The parts and percentages named in the examples refer to the weight. The K-values were each determined [at a percentage of] 1-percent in dimethyl formamide according to the specification of H. Fikentscher, Cellulosechemie 13, 58, (1932).

Example 1



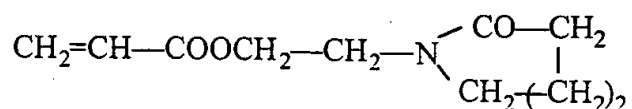
10.0 parts are heated for 4 hours to 60°C, under [a] nitrogen atmosphere and stirring with 0.1 parts azobisisobutyronitrile.

After precipitation with methanol, washing with methanol and drying, 9.3 parts of a polymer are obtained with a K-value of 76.5 (0.5% in dimethyl formamide), which has a

glass transition temperature T_G of +45°C and a refractive index n_D^{20} of 1.5006. The N-content is 9.0% (theoretical 9.04%).

Examples 2 to 12

Acrylic ester and

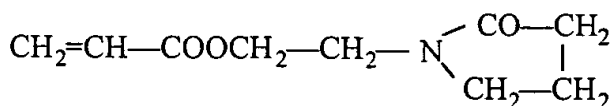


are mixed in certain ratios, transferred respectively with 0.1 percent by weight azobisisobutyronitrile and heated in the presence of 100 ml alcohol, for 2 hours at 70°C. The copolymers were dried through drying in the rotary evaporator and then in the vacuum drying cabinet for 10 hours at 60°C/12 torr. The results obtained are compiled in the following table.

No.	ethyl acrylate amount in parts	imido derivative	conversion %	K-value	%N	Proportion of the imido derivative in the copolymer in wt. %
2	9.9	0.1	90.0	86.0	0.05	0.8
3	9.5	0.5	84.0	85.5	0.3	4.5
4	9.0	1.0	86.0	91.0	0.6	9.0
5	8.5	1.5	86.0	89.0	0.9	14.0
6	8.0	2.0	86.0	87.0	1.4	19.6
7	7.0	3.0	89.0	89.0	1.9	28.0
8	6.0	4.0	93.0	88.0	2.5	37.5
9	5.0	5.0	97.0	88.5	3.2	48.0
10	4.0	6.0	98.0	89.0	3.7	56.0
11	2.5	7.5	97.0	88.0	4.8	72.5
12	1.0	9.0	100.0	79.5	5.8	87.5

Example 13

30 parts of



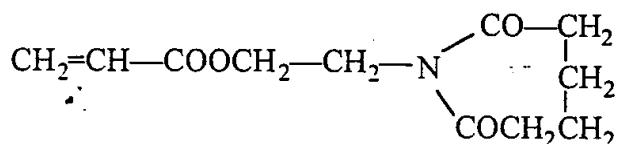
are mixed with 2 parts sodium pyrophosphate, 1.5 parts potassium persulfate, 2 parts of the sodium salt of a sulfonated fatty alcohol with 10 to 15 carbon atoms and 1000 parts

Translator: Andrea-Ingrid Schneider, 715-549-5734 (German #586/1997)

water. Pressed onto this mixture under stirring for 8 hours at 90°C is ethylene in amounts so that the pressure of the ethylene in the gas space is 285 atmospheres above atmospheric pressure. After a reaction time of 8 hours, the solids content of the dispersion is 19.5 percent by weight. The K-value of the copolymer is 36 (1% in decahydronaphtalene). The proportion of incorporated lactam is 4.9 percent by weight.

Example 14

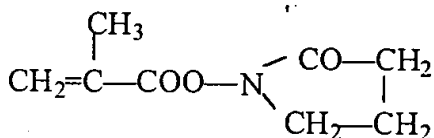
One proceeds the same as in Example 13, however, 30 parts of



are used. Furthermore, 170 parts of styrene are charged in place of ethylene. After a polymerization time of 8 hours, a dispersion results with a solids content of 16.5 percent by weight. The K-value of the copolymer is 52 (1% in toluene). The proportion of incorporated lactam is 15 percent by weight.

Example 15

One works as described in Example 13, however,



is used and ethylene is replaced by 80 parts of butadiene. At 90°C and a butadiene pressure of 6 atmospheres above atmospheric pressure, within 8 hours one obtains during the reaction time a dispersion with a solids content of 25.3 percent by weight.

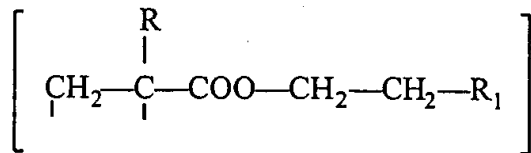
The K-value of the copolymer with an amount of 19.2 percent by weight of incorporated imide is 86.

Example 16

If one works as described in Example 9, but the acrylic ester is replaced by vinyl thioethanol $\text{CH}_2=\text{CH}-\text{S}-\text{CH}_2-\text{CH}_2-\text{OH}$, then a conversion of 89% is reached, a K-value of 69 and an amount of 47 percent by weight of incorporated lactam, corresponding to an N-content of 3.2%.

Patent Claims

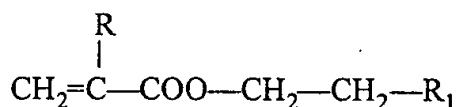
1. Polymers that are entirely or partially built from monomer units of the general formula



I

in which R represents hydrogen or a methyl group, and R₁ a cycloaliphatic lactam group.

2. Polymers according to claim 1, characterized in that in addition to the monomer units of the formula I, these comprise monomer units from other olefinic unsaturated monomers.
3. Process for the preparation of the polymers according to claim 1 or 2, characterized in that compounds with the general formula



(II)

in which R and R₁ have the meaning given in claim 1, possibly as mixture with other polymerizable monomers, are submitted to polymerization in the presence of radical forming initiators.

Badische Anilin- & Soda-Fabrik AG